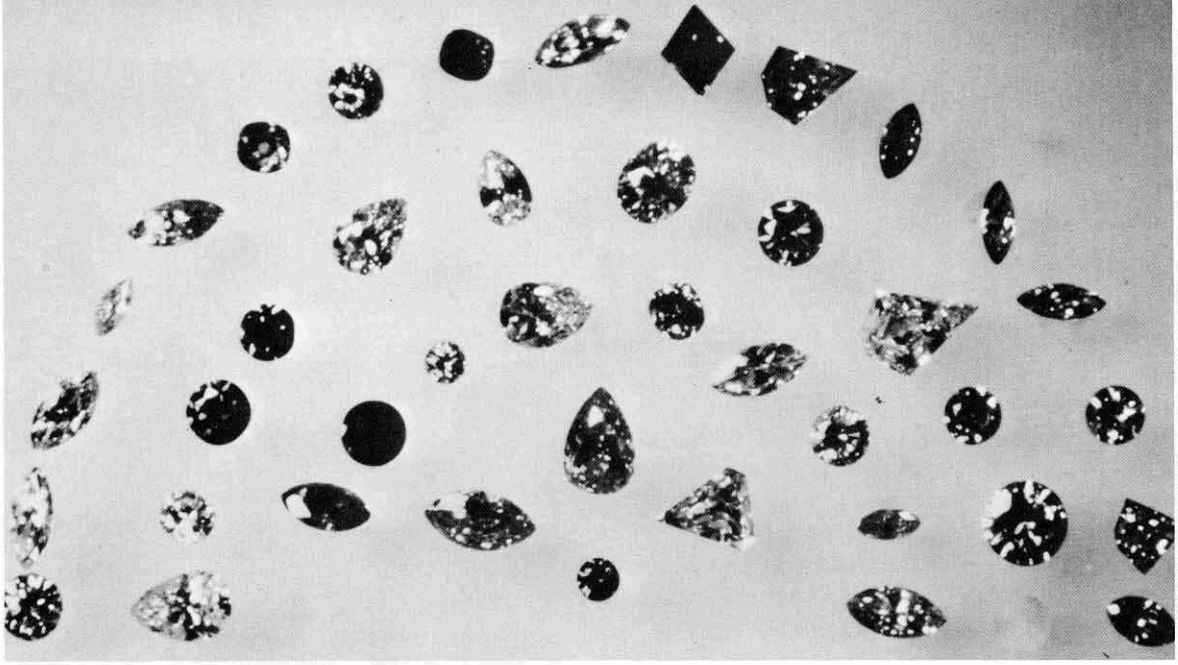


Glitter: Gems or Gyps?

The variations of color in minerals makes the difference between a valuable gem and a worthless stone. So, naturally, there are many ingenious ways to manipulate that color. A mineralogist describes some of the pitfalls that can accompany artificially colored gemstones.

by GEORGE R. ROSSMAN

From the earliest beginning of human history, mankind has been fascinated with the rocks and minerals of this planet, both for tools and for items of beauty. For centuries people have sought minerals that have certain characteristics they consider desirable—color, clarity, hardness, and rarity, for example. A mineral with these qualities is considered to be a gem.

It is the color that makes the difference between valuable gems and worthless stones. (Imagine a brown emerald or a pale pink ruby.) As a scientist, I try to study the origin of color in minerals and its relationship to other properties such as the chemistry or the structure of atoms.

The pyroxenes, for example, which are widely abundant in southern California, commonly exist as dull brown or black minerals except for one particular variety—jade. Most jade is composed of many different minerals, but one is present in abundance, and that is jadeite. This is the mineral that constitutes the bulk of precious Asian jade.

To understand the color of jade, you must delve a little bit into its chemistry. When jade is chemically pure, it is a sodium aluminum silicate. Each one of those individual constituents is incapable of causing color in the mineral, but as we all know, color does occur in jade. Obviously, the color must be due to the presence of other chemical entities.

One of the most important "impurities" in jade is the element iron. A very small amount of iron, typically 0.5 to 2 percent, can substitute for the aluminum of the jadeite, giving rise to the familiar soft green color of one variety of jade. The color of the most precious jade is brought about by the presence of the element chromium substituting for some of the aluminum. This causes a richer, more intense apple green color.

The presence of chromium is not the only way that jade can obtain a rich color, however. Jade specimens of inferior quality may be artificially dyed to bring

about a more desirable shade. How do you know, when you buy an item of jade, whether the attractive color is intrinsic to the jade itself or one that is brought about by human intervention? This is a problem we can address in the laboratory through the tools of science.

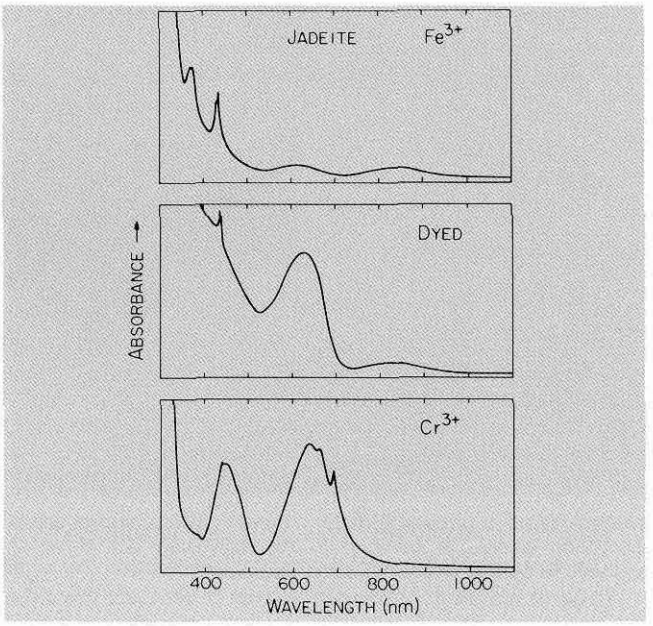
The chemicals used to dye things like jade are organic chemicals, in many respects similar to food coloring or coal tar dyes. They have certain characteristic properties, and with careful study, we can see properties in the color spectrum that allow us to determine whether or not the color is the chromium of natural precious Asian jade or whether it is simply a chemical.

We do this by quantitatively measuring the pattern of light absorption in a sample. We send a beam of light of different colors through the sample and monitor the intensity of light that is transmitted. A range of wavelengths from 400 to 700 nanometers covers the visible spectrum from violet to red. A sample of mineral that transmits light only in the 520-nanometer region will have the color green because both the red and violet are removed.

In the laboratory we extend the measurements beyond the range of visible light into the region of heat radiation, into the infrared region of about 1000 nanometers wavelength. The pattern we get consists of a series of absorption bands, and a high point on the curve means a high amount of light absorption by the sample.

When we compare a variety of samples of jade that have different coloring agents, we see differences in the patterns of light absorption. In a sample colored by the element iron, the pattern of absorption is typically weak. It consists of two broad absorption bands and then a sharp spike in the vicinity of about 400 nanometers. This contrasts sharply with a sample of jade that has been dyed, where we see a relatively strong absorption band in the area around 600 nanometers. A sample that has chromium in it shows a pattern with a sharp fine structure in the same region. Each of these patterns constitutes a diagnostic fingerprint by which to tell the origin of color in jade. It is thus simple to distinguish a dyed sample from a natural one.

Another stone that is sometimes dyed is turquoise. Turquoise is a copper-containing mineral, and the deep blue coloring of prime quality turquoise is brought about by the copper itself. But samples of a mineral called howlite can be dyed to make them look like turquoise. Very large nodules of howlite are mined,



The light absorption pattern makes a diagnostic fingerprint for determining which coloring agent is present in different samples of jadeite.

slabbed, soaked in dye, and sold as turquoise—sometimes labeled as dyed imitation turquoise.

You can readily tell the absorption pattern of genuine turquoise, using a spectrophotometer. But an even more interesting problem is to distinguish synthetic turquoise, which can be made entirely in the laboratory. It has the same chemical properties as natural turquoise, the color is the same, the density is the same, the hardness is the same. Even the absorption spectrum is the same in the visible region of light absorption. A manufacturer of synthetic turquoise even goes so far as to advertise that there is no way known to man to distinguish it from natural turquoise.

That sort of challenge appeals to me. So I tried to discover a way, and we did it in my laboratory using heat radiation in the infrared portion of the spectrum. We sent different wavelengths of heat radiation through a very small amount of a sample, scraped off the bottom of a stone, and looked at its absorption pattern. In a natural sample, there are several bumps and wiggles in the curve, and the fine structure shows sharp absorption peaks that are diagnostic of the absorption of heat radiation in natural turquoise.

In the synthetic sample, there is the same region of absorption, but the fine structure is relegated to very weak little shoulders on the absorption trace. The same

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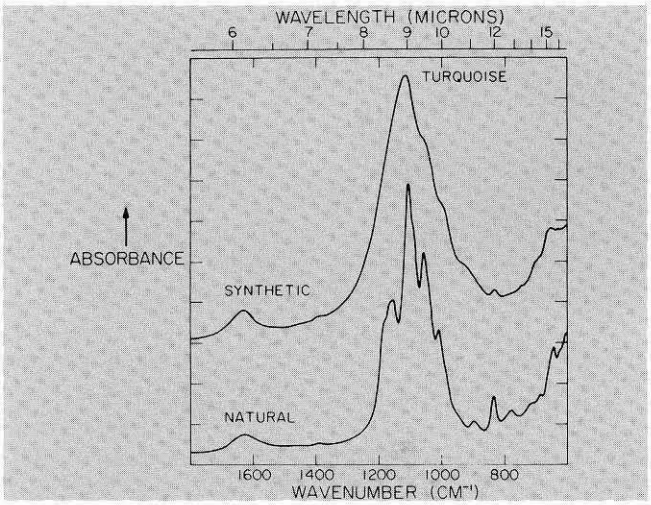


Infrared radiation passing through natural turquoise shows sharp absorption peaks, in contrast to the smoothed out curve of synthetic turquoise under the same treatment.

pattern appears in all samples of synthetic turquoise that we have examined, so this is a reliable method of distinguishing synthetic, grown-in-the-laboratory turquoise from the real thing.

A more challenging aspect of the field of mineral and gemstone coloration is represented by beryl, which is a comparatively obscure mineral, at least by this name. Chemically it is beryllium aluminum silicate. When no other element is present, beryl is perfectly colorless. But beryl also comes in colored varieties, which have such names as emerald, aquamarine, and morganite. The deep rich green of emerald is brought about by the presence of chromium substituting for a small amount of aluminum inside the emerald. About 0.1 percent by weight of chromium in a plus-three oxidation state is adequate to impart that color.

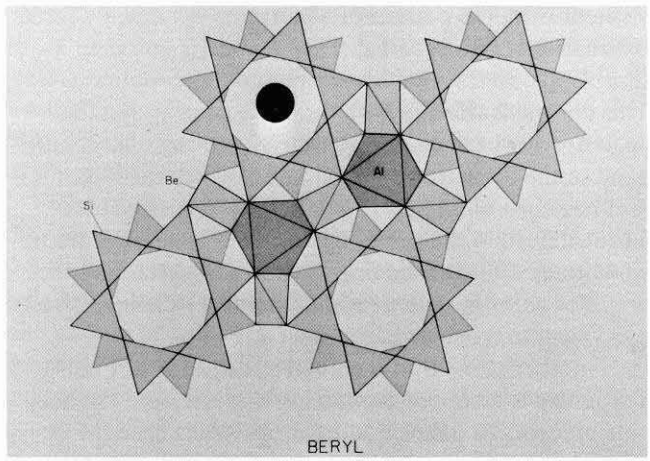
Morganite is a manganese-containing variety of beryl. If the manganese concentration is low, the color is very pale. When it is high, a spectacularly rich deep red morganite results. Unfortunately, it is seldom obtained in pieces large enough to be satisfactory for gem purposes.

A variety of beryl of great interest to me is aquamarine, which contains iron as the chemical impurity that imparts the color. Aquamarine comes in a wide variety of colors—brilliant golden yellow, yellow to yellow-green, and green, for example. The most desirable variety of aquamarine for gem purposes, however, is blue. Blue aquamarine is considered one of the birth stones, and is cut and fabricated into pieces of jewelry. But the chances are that if you have a piece of blue aquamarine, it did not start off life that way. Very early in the history of gems, the miners discovered that if they put their samples of, say, yellow beryl in charcoal stoves and heated them for a few hours, they would change from yellow into an attractive blue color. That is a widely applied very primitive technology.

What is there about the iron in beryl that gives rise to this variety of colors, and how does the application of heat change the color to blue? To answer this, we have to look at the atomic structure of beryl, in which there are three fundamental building blocks. First, there is an atom of aluminum that is surrounded by six atoms of oxygen, arranged in the geometry of an octahedron; second, an atom of beryllium, surrounded by four oxygens in the geometry of a small tetrahedron; and finally, an atom of silicon, also surrounded by four atoms of oxygen, and arranged in a larger tetrahedron. What we have to do is understand how these individual building blocks are assembled inside the crystal to form the structure of beryl.

What happens is that the silicons connect to form rings that stack up on top of each other in such a way as to define a soda-strawlike channel through the length of the crystal, and the iron that causes the color in beryl is located in those channels.

How does the iron inside the channels give rise to the transformation from yellow to blue under the heat treatment? The answer has to do with the oxidation of iron. As it is found in nature, yellow beryl contains a predominance of iron in the plus-three oxidation state;

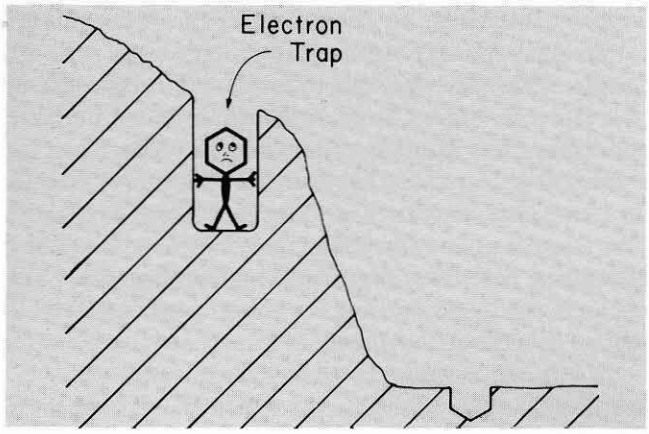


Silicon atoms in beryl form rings that stack on top of each other, forming soda-strawlike channels in the crystal. Iron in those channels causes the color in the mineral.

when the beryllium is heated in the charcoal furnace, the iron located in that channel is reduced to the plus-two oxidation state, gaining an electron and changing its color to blue.

Another example where heat treatment is used in the modification of gem colors is that of zircon. Zircon is a widely distributed mineral. In the chemically pure state it is zirconium silicate. It has value because it can be cut and fabricated into a colorless stone. But it also comes in a wide variety of colors, which indicates that impurities are present. The most important impurities for the coloration of zircon are uranium and thorium in amounts up to 0.5 percent.

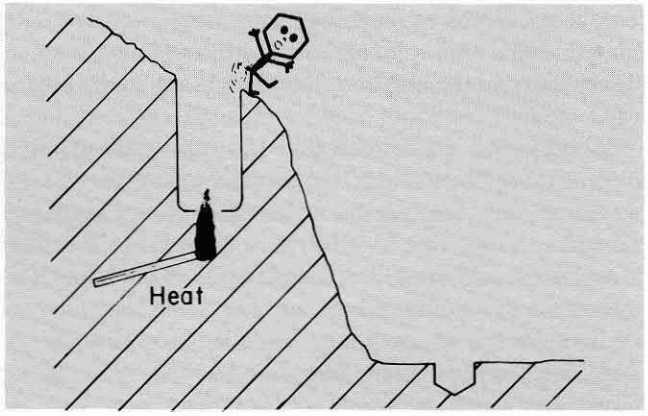
Zircon that contains uranium has a color ranging



When a gamma ray ejects an electron from an atom in a crystal, the electron loses energy and eventually comes to rest in an "electron trap" where it can absorb light and produce color.

from pale to deep amber-red. If these zircons are heated, some of the samples will become completely colorless, but a small proportion will turn a very beautiful blue, and will stay that color. What is the role of uranium in this process?

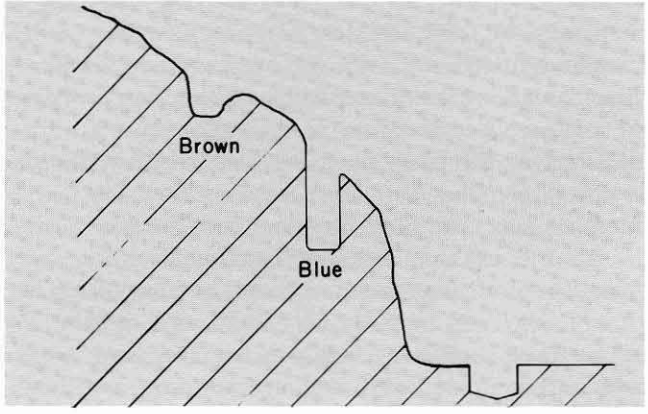
Uranium is a radioactive element, and as it slowly decays over many thousands of years, it liberates gamma rays, alpha particles, and electrons within the crystal. The gamma rays traveling through the crystal are so energetic they can take an electron from an atom of, say, oxygen and physically eject it. This electron will go cascading through the crystal, bouncing off atoms, and slowly losing its energy until it finally comes to rest in what I call an "electron trap." The electron wants to be back on the oxygen, but it can't get out of the trap. Inside that trap it has the ability to absorb light, to produce color within the crystal.



One way to change the color of a mineral is to get the electrons out of the trap by applying heat. If you apply enough heat, the mineral may become colorless.

Technically speaking, what this electron trap may be is the combination of one of the electrons near an adjacent zirconium with some other chemical impurity within the crystal. Another possibility is that an electron may go wandering through the crystal lattice, bouncing off different atoms until it comes to rest in a defect—a missing atom—where it sits absorbing light and giving color to the crystal.

We can get the electron out of the trap with the heat treatment. If you apply enough heat, all the electrons can be totally removed from the traps, and the zircon will become colorless. Very often, however, there are multiple traps, and if an electron is stuck in a particular one, it will impart a brown color to the crystal. If it's stuck in a much deeper trap, it will impart a blue color. If we very carefully control our heat treatment, we can



Often there are multiple electron traps in a mineral. When the brown trap is shallower than the blue, carefully controlled heat treatment may make it possible to keep the blue color.

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remove the electrons from the brown trap—because it's relatively shallow—and at the same time we can keep the majority of the electrons where they are in the blue trap.

Spodumene is a mineral found in gem mines in San Diego County, near Pala. It is actually one of the pyroxenes, lithium aluminum silicate. It comes in two colored varieties, one of which is called kunzite. Kunzite contains a small amount of manganese, which imparts a lavender color in minerals. A second, much less common variety of spodumene is called hiddenite. It contains chromium as the impurity, and the color that is imparted is green. A sample of raw kunzite would probably sell for less than a dollar a carat; a sample of gem-quality hiddenite would probably sell for about a thousand dollars a carat. Understandably, there is a significant financial incentive to come up with a technological way of changing kunzite to hiddenite.

I took a sample of kunzite to JPL and irradiated it with cobalt-60 for many, many hours. It soaked up enormous intensities of radiation, but it did not become radioactive. The treatment is as harmless as sending light rays through a sample, but it does send those electrons on the move and into the traps. When I took the sample out of the irradiator, I found I had indeed changed lavender spodumene into green spodumene. This looks like a good deal, because presumably I could sell these stones and make a huge profit. If I do, I had better take my money and leave the country, because this is a gyp. The color of that green stone will spontaneously fade in a matter of a week. It won't fade back to lavender; it fades to colorless.

Well, I got some interesting science out of this. I learned that the color changes have to do with changes in the oxidation state of the manganese. Lavender kunzite starts off with manganese in the plus-three oxidation state. Exposure to gamma rays oxidizes the manganese to plus-four. In the fading process, electrons are gained by the manganese, which goes back to manganese plus-two, which is pale yellow. It's interesting chemistry but very poor economics.

Another example is that of topaz, which is a typically colorless aluminum silicate. In a few places in Utah, the Soviet Union, Brazil, and Mexico, samples can be found that have a lovely amber to cinnamon-red color. These stones constitute imperial topaz, and they are cut to gems.

The color of topaz is induced in nature by the presence of radiation. Everything in the ground has a very small amount of radioactive elements. Over hundreds of thousands of years, crystals of minerals sitting inside cavities in rocks soak up this feeble radiation, generating the color that you see. If you subject a sample of colorless topaz to irradiation, it will change to the color of imperial topaz. But again, you have the problem of fading. I put a sample of irradiated topaz on the roof of my laboratory, and within a day all the color was lost. I put it into the cobalt-60 irradiator, and within half an hour the color was back. So, light is another way to get the electron out of the electron trap.

With topaz, however, the story doesn't end there. For a very small percentage of topaz that is irradiated and then carefully heated, something marvelous happens. It turns blue—permanently. This blue color is extremely desirable for gems; in fact, blue topaz is a gemstone that dates back to ancient times. It is possible to create a blue topaz by an artificial laboratory process, and the result is identical to natural blue topaz. The chemistry is the same, and so are the optical properties, the density, and a variety of other properties. Artificial blue topaz is essentially indistinguishable from natural blue topaz, because in this case the laboratory technician is exactly duplicating the coloring agent that is present in natural blue topaz.

If it is important to do so, how do you tell them apart? Well, this is Caltech, so we took on answering that question as a challenge.

The electron sitting in a trap is really in a site of higher energy than normal. Sunlight or heat has the ability to remove the electron from its trap, but in the process the electron has to dissipate its excess energy. It can do this in two ways. One is to make the crystal warm. Crystals that have been intensely irradiated often feel warm to the hand because of the electrons moving back toward the place they want to be. The second way for the electron to dissipate its energy is in the form of light.

Technically speaking, the electrons in the crystal returning to the site from which they came commonly transfer some of their energy to a small amount of some impurity inside the crystal. The light that you can see is the glow of the impurity, and the name for the phenomenon is "thermoluminescence," that is, light caused by heat. There are ways of observing this glow under carefully controlled laboratory conditions that allow us to utilize thermoluminescence as a method of detecting samples of minerals that have been irradiated.

We place the crystal in some sort of heating apparatus, and we then simultaneously monitor the temperature of the sample and look at the light that is emitted from it, collecting it with a photomultiplier tube, a light detector. A chart recorder takes the signal and makes a graph of the intensity of light given off as a function of the temperature of the sample. If we see thermoluminescence, we know absolutely certainly that the sample has a history of radiation treatment, either in a laboratory or in nature. Furthermore, if a sample of topaz has been heated in a laboratory to a temperature high enough to bleach out the brown color, the low-temperature thermoluminescent electron traps will have been removed in the process.

When we compare natural blue topaz and artificially irradiated blue topaz, we get two distinctly different curves. The natural sample will show thermoluminescence at a temperature somewhat above 200 degrees. But the glow of the artificially heat-treated sample does not begin until a somewhat higher temperature and shows all sorts of different higher temperature electron traps. This is a very simple way of differentiating between artificially treated and natural blue topaz. To do so requires a sample quantity so small that a cut and faceted gemstone can be scraped on its edge to acquire a few grains, and there will be no damage to it.

What about irradiating other minerals? If you irradiate halite, which is common table salt and colorless in nature, it turns amber. If you irradiate it still more, it turns black. This could raise the interesting possibility of serving black table salt, but I don't think anyone intends to use water-soluble salt as a gemstone.

Common old silicon dioxide—sand or quartz—is colorless in its chemically pure state. When either man or nature irradiates it, it turns dark. This is done commercially to form smoky quartz. Natural smoky quartz contains aluminum as an impurity, and natural irradiation develops the brownish-black color. Colorless natural quartz that contains aluminum but has not been subjected to natural radiation can be artificially irradiated to produce smoky quartz, and I've seen it for sale at a variety of places.

If iron instead of aluminum is the impurity in quartz, treating it will produce amethyst, but because of the abundance of amethyst in nature, there's no economic incentive to produce it artificially.

Rubies and emeralds are not subject to radiation treatment in the laboratory. You get them naturally and that's it. Both, however, are readily synthesized in the laboratory. Sapphires are also readily synthesized, so there's no economic incentive to do radiation coloration. A small amount of heat treatment is occasionally used to enhance the color of blue sapphire. Yellow varieties of sapphire can be spectacularly enhanced in color by radiation, but they quickly fade. This is surprising because natural yellow sapphires are perfectly stable.

You've probably been led to believe that diamonds are colorless, or at best blue-white. This is the result of advertising by the gem industry. Diamonds come in a variety of colors—yellows, blues, reds, greens, and all sorts of intermediate shades. Irradiated diamonds are things of beauty. Is the color stable? Well, we all know a diamond is forever.

This again brings up the question of whether synthetic or artificially enhanced minerals are gems or gyps. Obviously, if a product is misrepresented, it is a gyp. And in the area of fine gems purchased as investments, the need for caution is great. Fortunately for the consumer, the reputable gem industry is deeply concerned with its image and its integrity. The industry maintains its own research programs into methods for establishing the origin of color in gems and makes frequent use of the type of information scientists generate in their study of minerals.

Materials that are not of investment caliber must be considered as a separate case. Such materials would be purchased primarily for their beauty, and in this case the value is in many ways subjective. For the person who demands only natural color, and is willing to pay the price, sufficient safeguards have been developed generally to protect the customer. But as the demand for gems increases, the supply will become depleted and the costs will rise. It is here that technology can increase the supply and keep costs down by transforming ordinary minerals into items of beauty. The scientists who design these processes are concerned with producing valuable products that will be acceptable to the public, and their products are absolutely indistinguishable from naturally colored stones except by methods available only to specialists. The beauty, color, and durability of such technologically produced gems are equal to, and in some cases superior to, naturally colored stones. In fact, the lab technician is generally duplicating in minutes the exact processes that nature takes tens of thousands to millions of years to accomplish. My own answer to the question is that these are indeed gems. □